

Autoclaving treatment of wasted disposable bamboo chopsticks



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ABSTRACT

The autoclaving combined with mechanical separation, known as the mechanical heat treatment, is one of the promising alternatives to treat the mixed wastes consisting of organics and inorganics. After autoclaving, the organics can then be sorted, separated and recovered for the re-utilization. In this study, the steam autoclaving of bamboo chopstick (BC), which is one of the major biomasses in the municipal solid waste, was performed. The effects of steam autoclaving temperature (T) and autoclaving reaction time (t) on the characteristics of BC were examined. The thermal gravimetric and differential thermogravimetric analyses were conducted to assess the pyrolysis behavior of autoclaved BC which can be further treated to produce up-graded refuse derived fuel or bio-char. The results indicated that the autoclaving extent of BC ($= (\text{initial mass} - \text{mass at } t) / \text{initial mass}$, in dry basis) increases with increasing T and t . The high heating value per mass in dry basis (H_{HMD}) of raw BC after autoclaving increases from 4365 kcal/kg to about 4975 kcal/kg at $T = 428$ K with $t = 60$ min (A428-60) and to 5044–5158 kcal/kg at 453 K with 30 (A453-30) and 60 min (A453-60), enhancing the energy densification ratio (ratio of H_{HMD} after to that before autoclaving) to 1.06–1.17. However, on the wet basis, the water content of autoclaved product for the case of A428-60 is 35.85 wt.% being less than those of A453-30 and A453-60 of 45.33–55.20 wt.%. The comparison indicated that the conditions at 428 K with 60 min are more appropriate than the others, giving satisfactory H_{HMD} with less water content. The pyrolysis behaviors of autoclaved BCs employing $T = 428$ –453 K and $t = 15$ –60 min are closed to that of raw BC, thus retaining the pyrolytic quality of BC. The information obtained in the present study is useful for the rational design and proper operation of autoclaving system for treating the wasted BC.

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1. Introduction

To reach the ultimate goal of comprehensive recycling and reuse without significant waste, mechanical heat treatment (MHT), which involves autoclaving and mechanical separation, has been assessed for the sorting of recyclables (metals, plastics and glass), floc/fiber and rejects from municipal solid waste (MSW) [1–10]. Autoclaving is essentially a pressurized thermal process performed in a closed vessel at high temperature under high pressure. Holloway [1] applied 138–689 kPa steam to 1.9 cm

diameter perforated drum for 20–120 min to treat the waste material. The process produced sterilized organics and recyclable inorganics. The sudden depressurization at final stage can separate organics and inorganics well. For organics, the liquid part can be separated easily while the solid part with 13% moisture can be used as feedstock for fermentation with enzyme addition. For inorganics, the ferrous and non-ferrous parts can be separated through magnets. The final rejects were disposed to landfill. Eley and Holloway [2] added 0–0.33 kg $\text{H}_2\text{O}/\text{kg}$ MSW to the vessel with pressure of 101–414 kPa for the screened domestic wastes. The optimal pressure is 276 kPa, resulting in a volume reduction of 57%. All of the solid fractions after the treatment were screened by 5.1 and 1.3 cm screens in series. About 80–90 wt.% of the metals are in the 5.1 cm fraction. For plastics, about 60, 40 and 0.5 wt.% are in the 5.1, 1.3–5.1 and less than 1.3 cm fractions, respectively. As for glass and ceramics, the fractions in the 5.1, 1.3–5.1 and less than

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1.3 cm are about less than 1, 8.0 wt.% and remainder, respectively. About 20 and 80 wt.% of the cellulosic and food wastes are in the 1.3–5.1 and less than 1.3 cm fractions, respectively. Eley [3] further examined the chemical compositions of the screened parts. These included the heavy metal contents, chemical oxygen demand (COD), biological oxygen demand (BOD), ammonium nitrogen and total Kjeldahl nitrogen (TKN). The results showed that the heavy metal contents are permitted for compost application. For further compost treatment, extra nitrogen should be added.

The floc/fiber obtained after MHT is mainly composed of kitchen waste, paper and woody waste. It can be further reprocessed for recycling application, producing up-graded refuse derived fuel (RDF) or biological treating to obtain compost-like output as suggested by Eley [3]. The estimated market size was reported to reach 0.3–0.6 million tons/yr (or t/yr) in England during 2007 [4,5]. For the use of RDF from floc/fiber as co-fuel of coal fired power plants and cement kilns, the comparative high calorific value of RDF (also noted as solid recovered fuel (SRF)) of 15–18 MJ/kg (=3580–4296 kcal/kg with 1 cal = 4.19 J) can reduce the global warming and acidification impacts significantly with less consumption of fossil fuels [6]. Papageorgiou *et al.* [7] compared three MSW treatment technologies (mass burn incineration (MBI), mechanical biological treatment (MBT) and mechanical heat treatment (MHT) to assess their economic benefits and carbon emission. The MBT and MHT can output bio-gas and RDF, respectively to replace fossil fuels. Both MBT and MHT can reduce the greenhouse gases (GHG) emission for the end usage of fuel.

Chang *et al.* [8,9] applied the MHT to separate the organic parts from MSW for the case study in Taiwan. For the examination of the effects of autoclaving on the properties of the recovered products, Hung *et al.* [10] performed the autoclaving of individual materials of toilet, news and thick plate papers. Although the mass of autoclaved material decreases, however, its heating value is retained substantially. Thus, the recovered organics (*i.e.*, floc/fiber) can be processed to produce RDF or bio-char for further uses as feed of thermal-chemical processes of pyrolysis, gasification and combustion [11,12]. These processes have been also commonly applied for the utilization of bio-wastes and biomass so as to match the appeal of resources reutilization and/or carbon reduction [13–19].

In the woody waste, the wasted disposable chopsticks (WDCs) are abundant in Taiwan due to the widely use of chopsticks for the prevention of Hepatitis B. Most chopsticks in Taiwan are made from wood or bamboo chips weighted about 7.95 g per pair [20]. In 2008, about 50 billions pairs of wood and bamboo chopsticks were used [21], counting for 39,750 t/yr waste. This study examined the performance of autoclaving of bamboo WDCs (WDBC). The thermal-chemical characteristics of WDBC before and after autoclaving were elucidated. The beneficial feasibilities for the further use of autoclaved WDBC as good-quality RDF and bio-char were also evaluated.

2. Experimental methods

The raw bamboo chopstick (BC) purchased from Dong-Cheng Co. (Taipei, Taiwan) was used to simulate the WDBC. The hemi-cellulose (HC, crude from aspergillus), cellulose (CE, powder microcrystalline) and lignin (LG; dealkaline, reagent grade) employed for comparative tests were supplied by Sigma–Aldrich Co. (St. Louis, Missouri), MP Biomedicals Co. (Illkirch, France) and Nacalai Tesque Inc. (Kyoto, Japan), respectively.

The WDBC was treated using laboratory-scale autoclaving device shown in Fig. 1. The device is mainly composed of a pressurized boiler (600 mL) filled with 500 mL de-ionized (DI) water to supply saturated steam and another pressurized autoclave reactor (1500 mL) with wire-net stirrer filled with

40 g WDBC of 2-cm length. The stirring speed of stirrer (N_R) was at 350 rpm. The major variables examined were steam temperature ($T = 428$ and 453 K) and autoclaving reaction time ($t = 15$, 30 and 60 min). The moisture, and ash and combustibles (CBs) contents were analyzed by TEPA methods NIEA R213.21C [22], and NIEA R205.01C [23], respectively. The cellulose CE and hemi-cellulose HC were analyzed following TAPPI methods T203 om-93 [24] and T223 om-01 [25], respectively. The Klason lignin LG was measured via TAPPI T222 om-02 [26]. The calorific value or high heating value per mass in dry basis (H_{HMB}) was determined using Parr calorimeter (Oxygen bomb plain jacket calorimeter, model 1341; Ignition unit 115/50/60, model 2901EB; Digital thermometer assay 6775, Model A360C; Parr Instrument Co., Moline, IL) according to ASTM D2015 [27]. The elemental analysis was conducted employing the element analyzer (Elementar Vario EL-III, Hanau, Germany) following TEPA NIEA R409.21C [28]. The thermal gravimetric analysis (TGA) and differential thermo-gravimetric (DTG) measurements were performed using Shimadzu TGA-51H (Shimadzu Co., Kyoto, Japan). The TGA records the variation of mass or residual mass fraction M with T . The differential of M with T then gives $-dM/dT$ vs. T .

3. Results and discussion

Table 1 shows the composition and weight changes of BC, LG, CE and HC after autoclaving under different conditions. As expected, the un-autoclaved raw BC (denoted as Case UA) consists mostly the combustibles of 93.61 wt.%, which are essentially composed of the volatiles of 93.27 wt.%. The fixed carbon is of negligible amount of 0.34 wt.%. Both the percentages of dry-basis weight reductions of BC (R_{mBCD}) and combustibles of BC (R_{CBBCD}) increase as autoclaving time t increases. The R_{mBCD} and R_{CBBCD} are closed, indicating that the dry-basis weight reduction is mostly contributed by the combustibles during the autoclaving. Further, the extent of autoclaving of BC, which is defined as the ratio of the difference of initial mass (m_0) and mass at t (m_t) to m_0 in dry basis, is more vigorous at a higher temperature. Moreover, the moisture content of autoclaved solid product at 428 K increases as t increases from 15 to 30 min. All these are consistent with the cause that longer time and higher temperature enhance the extent of hydrolysis reactions by autoclaving. However, it is interested to note that the moisture contents of autoclaved solid products at 428 K and 453 K decrease as t further increases from 30 to 60 min. This may be due to the cause that some water content in solid further participates in the autoclaving reactions or the hydrophilic property of product decreases as t is prolong.

Table 1 also illustrates the effects of autoclaving on the contents of the LG, CE and HC of BC. The un-autoclaved raw BC contains a high content of CE of 52.59 wt.% in dry basis. The secondary constituent is LG with content of 31.75 wt.%, indicating that the recovered BC is suitable for further processing such as torrefaction to produce the bio-char containing high LG. As t_R increases, the percentages of dry-basis weight reductions of LG (R_{LGBCD}), CE (R_{CEBCD}) and HC (R_{HBCD}) all increase because the reaction extent becomes higher for longer t . Except in the short t of 15 min, the HC is generally easier to be hydrolyzed and reacted than the CE and LG as reflected by the polymerization extents of their polymer structures. This phenomenon is more pronounced for vigorous autoclaving at high T of 453 K and long t of 60 min, however, still keeping 58.44, 83.35, and 81.50 wt.% of HC, CE and LG. For mild autoclaving ($T = 428$ K, $t = 15$ –60 min; $T = 453$ K, $t = 30$ min), most of HC, CE and LG are preserved, retaining 74.29–93.91, 87.54–88.95 and 83.39–87.74 wt.%, respectively. The residual liquid contains the hydrolysis by-products of LG, CE and HC during autoclaving. It is noted that the contents of LG, CE and HC of BC of 31.75, 52.59 and 11.78 wt.% of this study are qualitatively analogous to those of

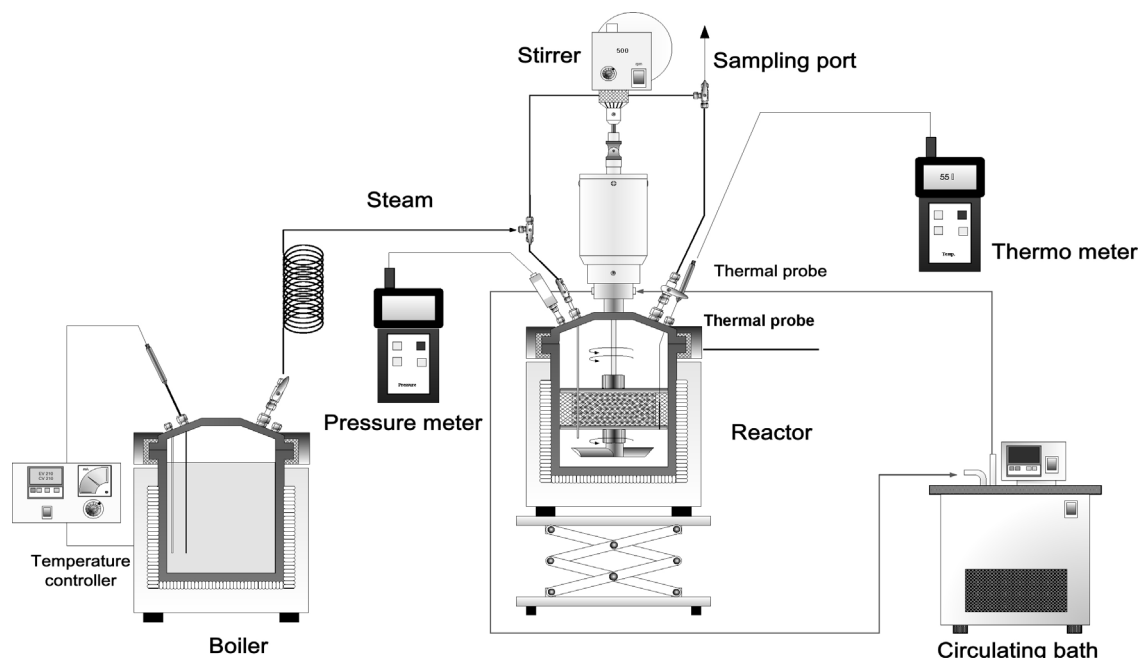


Fig. 1. The laboratory-scale autoclaving device for WDBC treatment.

garden waste of 45.03, 38.28 and 5.9 wt.% examined by Chang et al. [8]. Their results indicated that the pH value, conductivity, COD and TOC of residual liquid after autoclaving are about 4.18–4.69, 6.61–11.06 $\mu\text{S}/\text{cm}$, 2×10^4 to 2.76×10^4 mg/L and 1.18×10^4 to 2.91×10^4 mg/L, respectively. Thus, the residual liquid of autoclaving of BC might exhibit low pH value, while contain compounds contributing the increase of conductivity, COD and TOC.

Table 1 further depicts the variations of proximate composition of combustibles, moisture and ash and weight of BC with the temperature–time (T – t) value, which reflects the power consumption. The ultimate goal of autoclaving is to achieve the easy separation of products while to retain or enhance their valuable qualities such as combustibles content and high heating value per mass in dry basis H_{HMD} with less energy consumption. Thus, the results indicated that the appropriate conditions revealed in this

study for the autoclaving of BC are at 428 K with 60 min (Case A428-60 with T – $t = 25,680$ K min) giving high combustibles of 63.42 wt.% while low ash and moisture of 0.73 wt.% and 35.85 wt.%, respectively. The product at 428 K and 60 min preserves about 84.11 wt.% CBs ($=1 - \text{magnitude of } R_{\text{CBCD}}$ in Table 1 $= (100 - 15.89)$ wt.% = 84.11 wt.%). The conditions at 453 K with 30 min (Case A453-30 with T – $t = 13,590$ K min) result in about the same dry-basis weight changes of BC and combustibles as Case A428-60. Although Case A453-30 even consumes lower T – t (13,590 K min) than Case A428-60 (25,680 K min), however, it gives higher moisture content.

Table 2 lists the H_{HMD} of BC after autoclaving with steams at various times and temperatures. The H_{HMD} of BC after autoclaving are preserved. The average values of H_{HMD} at 428 K for 15–60 min and at 453 K for 30–60 min are about 4644.33 and 5100.97 kcal/kg,

Table 1
Proximate composition and weight changes of bamboo chopstick (BC), lignin (LG), cellulose (CE) and hemi-cellulose (HC) after autoclaving with steams at various temperatures (T) and times (t).

Item	Un-autoclaved Raw, Case UA	Autoclaved				
		428 K			453 K	
		15 min, Case A428-15	30 min, Case A428-30	60 min, Case A428-60	30 min, Case A453-30	60 min, Case A453-60
Moisture ^a (wt.%)	4.21	42.11	57.69	35.85	55.20	45.33
Ash ^a (wt.%)	2.18	1.10	1.32	0.73	0.84	1.83
Combustibles ^a (wt.%)	93.61	56.80	40.99	63.42	43.96	52.84
Volatiles ^a (wt.%)	93.27	56.53	40.97	63.35	43.93	52.79
Fixed carbon ^a (wt.%)	0.34	0.27	0.02	0.07	0.03	0.05
R_{mBCD} of BC ^b (wt.%)	NA ^d	–3.59	–9.60	–16.86	–15.61	–18.37
R_{CBCD} of combustibles ^b (wt.%)	NA	–3.22	–10.37	–15.89	–15.27	–19.27
LG ^b (wt.%)	31.75	28.13	29.29	27.71	32.33	31.70
CE ^b (wt.%)	52.59	48.53	57.81	55.48	53.44	53.70
HC ^b (wt.%)	11.78	11.48	10.17	10.53	10.23	8.44
R_{LGBCD} of LG ^b (wt.%)	NA	–14.60	–16.61	– ^e	–12.26	–18.50
R_{CEBCD} of CE ^b (wt.%)	NA	–11.05	– ^e	–12.30	–12.46	–16.65
$R_{\text{HCB CD}}$ of HC ^b (wt.%)	NA	–6.09	–22.00	–25.71	–25.24	–41.56
T – t value ^c (K min)	NA	6420	12,840	25,680	13,590	27,180

^a Wet basis.

^b Dry-basis weight changes of BC (R_{mBCD}), combustibles (R_{CBCD}), LG (R_{LGBCD}), CE (R_{CEBCD}) and HC ($R_{\text{HCB CD}}$), respectively.

^c T – t : multiplication of T and t .

^d NA: not applicable.

^e –: not computed.

Table 2Changes of high heating value per mass in dry basis (H_{HMD}) and elemental composition of BC after autoclaving with steams at various times.

Item	Un-autoclaved Raw, Case UA	Autoclaved				
		428 K		453 K		
		15 min, Case A428-15	30 min, Case A428-30	60 min, Case A428-60	30 min, Case A453-30	60 min, Case A453-60
H_{HMD}^a (kcal/kg)	4365.23 (73.61) ^c	4602.01 (167.02)	4356.10 (106.90)	4974.86 (40.32)	5157.60 (82.70)	5044.34 (205.22)
Element ^b (wt.%)						
N	0.320 (0.003)	0.295 (0.011)	0.318 (0.001)	0.314 (0.007)	0.254 (0.020)	0.354 (0.037)
C	44.862 (0.832)	45.243 (0.261)	44.234 (0.104)	45.819 (0.125)	47.670 (1.234)	49.206 (0.351)
S	1.140 (0.286)	0.606 (0.129)	0.489 (0.013)	0.385 (0.013)	0.890 (0.217)	0.245 (0.012)
H	6.411 (0.096)	6.468 (0.127)	6.561 (0.028)	6.381 (0.142)	6.435 (0.025)	6.246 (0.138)
O (balance)	47.267	47.389	48.399	47.103	44.752	43.951
H/C (wt./wt.)	0.143	0.143	0.148	0.139	0.135	0.127
O/C (wt./wt.)	1.054	1.047	1.094	1.028	0.939	0.893
T-t value (K min)	NA ^d	6420	12,840	25,680	13,590	27,180

^a H_{HMD} = high heating values per mass in dry basis.^b Dry basis.^c Numbers in parentheses are standard deviations of σ_{n-1} .^d NA: not applicable. T-t: as specified in Table 1.

respectively. Comparing these values with the H_{HMD} of 4365.23 kcal/kg of un-autoclaved raw BC indicated mild increase of energy densification ratio (E_D , ratio of H_{HMD} after to that before autoclaving) after autoclaving, giving E_D of about 1.06–1.17. Although some combustibles were hydrolyzed during autoclaving, however, a large portion of contents with higher heating value were preserved than those with lower heating value. For example at 453 K with 60 min, the R_{LGBCD} of lignin of 18.50 wt.% as well as R_{CEBCD} of cellulose of 16.65 wt.% is less than the $R_{\text{HCB CD}}$ of hemicellulose of 41.56 wt.% as shown in Table 1.

Table 2 also gives the elemental composition of BC after autoclaving. The variation of composition of carbon C exhibits slight increase for the cases at 428 K with 60 min (Case A428-60) and 453 K with 30 and 60 min (Cases A453-30 and A453-60). The increase of carbon content certainly contributes to the increase of energy densification ratio E_D . On the other hand, the contents of H and O decrease at 428 and 453 K with 60 min (Cases A428-60 and A453-60). Therefore, a long autoclaving time reduces the contents of H and O. The S content decreases as autoclaving time increases. This is due to the cause that some sulfur-containing compounds are hydrolyzed by autoclaving reaction. Table 2 further illustrates the weight ratios of H/C and O/C at various autoclaving conditions. The H/C and O/C are reduced for Cases A428-60 and A453-60. The reduction of H/C and O/C in turn assists the followed processing such as torrefaction.

Fig. 2 presents the DTG diagrams of un-autoclaved raw BC at various heating rates (HRs). At low HRs of 5 and 10 K/min, the results both exhibit two apparently high peaks at around 600 and

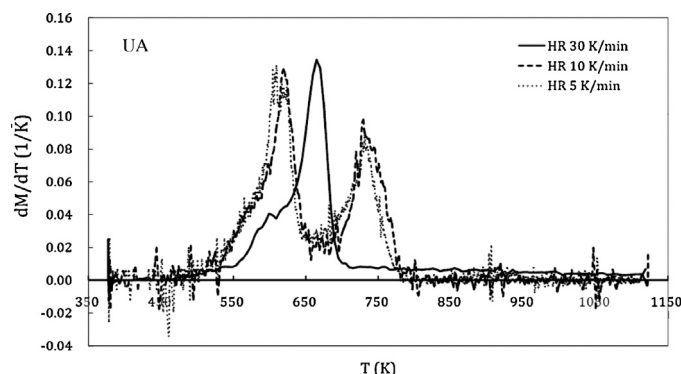


Fig. 2. DTG diagram of un-autoclaved raw BC (Case UA) at various heating rates (HRs). Residual mass fraction $M = W/W_0$; W_0 and W : initial mass and mass at T .

730 K, revealing the thermal decompositions of components of HC and CE of BC. The HC is more easily decomposed with the peak appears earlier than the CE. The decomposition of LG needs more energy while with slow decomposition rate, resulting in a wider temperature range for pyrolysis with low peak value. At high HR of 30 K/min, the pyrolysis is vigorous, resulting in the closed occurrence of peaks of pyrolysis rates of HC and CE and thus exhibiting one overlapped peak for the pyrolysis rate of un-autoclaved raw BC. For supporting these points, the DTG characteristics of sole HC, CE and LG are demonstrated with HR = 30 K/min as shown in Fig. 3, indicating closed occurrence of rate peaks of HC, CE and LG at around 630–670 K in consistence with that of un-autoclaved raw BC at around 670 K. The peak values of HC and CE are much higher than that of LG, further supporting that the pyrolysis is essentially aimed at removing of HC and CE while retaining LG. Furthermore, the peak rates of pure HC, CE and LG are also faster than that of BC with mixed HC, CE and LG, reasonably indicating that pure HC and CE are much easy for pyrolysis than mixed HC and CE in BC. The corresponding TGA curves of Fig. 3 are shown in Fig. 4, revealing the order of easiness of pyrolysis as $\text{HC} > \text{CE} > \text{LG}$. The pyrolysis of HC is essentially accomplished in 600–680 K with residual mass fraction M decreasing from 0.95 to 0.2. For the CE, M reduces from 0.95 to 0.14 in 630–700 K. As pyrolysis proceeds further longer, it results in the formation of residual carbon, which is about 5 wt.% relative to the initial mass at about 1120 K. For the LG, the pyrolysis takes place very slow, reducing M to 0.7 at 700 K. The slow pyrolysis of

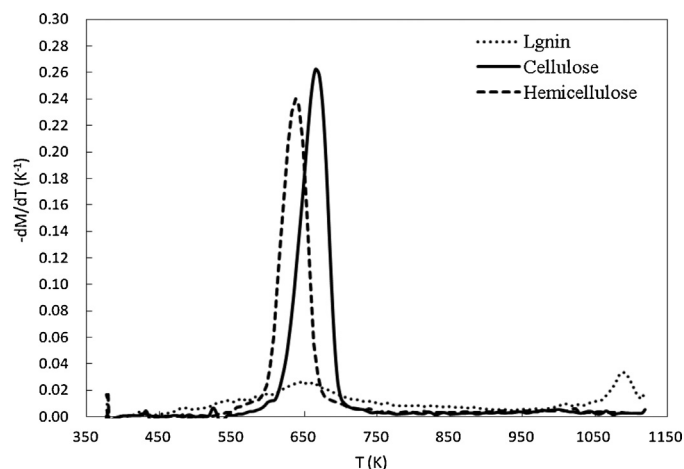


Fig. 3. DTG curves of hemicellulose, cellulose and lignin at HR = 30 K/min.

LG, on the other hand, supports the torrefaction of LG-containing material at moderate temperature which can retain more LG while remove more HC and CE.

Figs. 5 and 6 illustrate the TGA and DTG curves of autoclaved BCs at HR = 30 K/min, respectively. At the mild autoclaving conditions for Case A428-15 ($T = 428$ K, $t = 15$ min), their TGA (Fig. 5a) and DTG (Fig. 6a) are closed to those of un-autoclaved raw BC. Thus, the quality of mild autoclaved BC for further pyrolytic treatment is essentially retained. As for the vigorous autoclaving

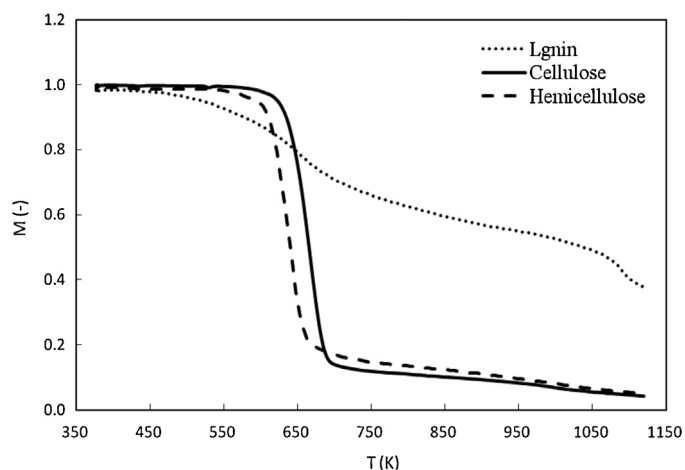


Fig. 4. TGA curves of hemi-cellulose, cellulose and lignin at HR = 30 K/min.

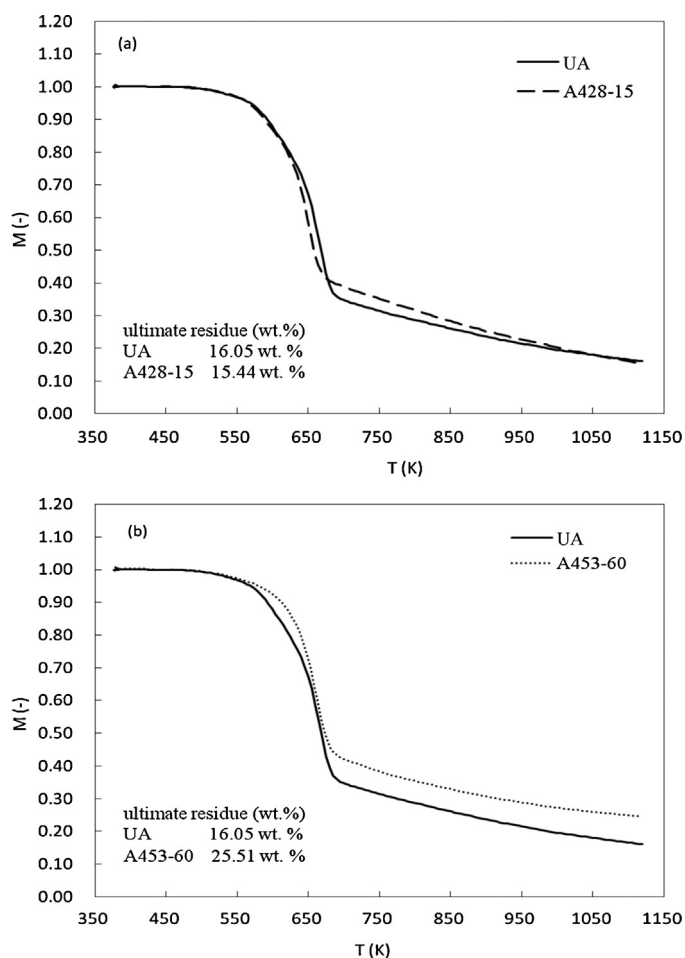


Fig. 5. TGA curves of autoclaved BCs. UA: un-autoclaved raw BC, HR = 30 K/min. (a) and (b) Cases A428-15 and A453-60.

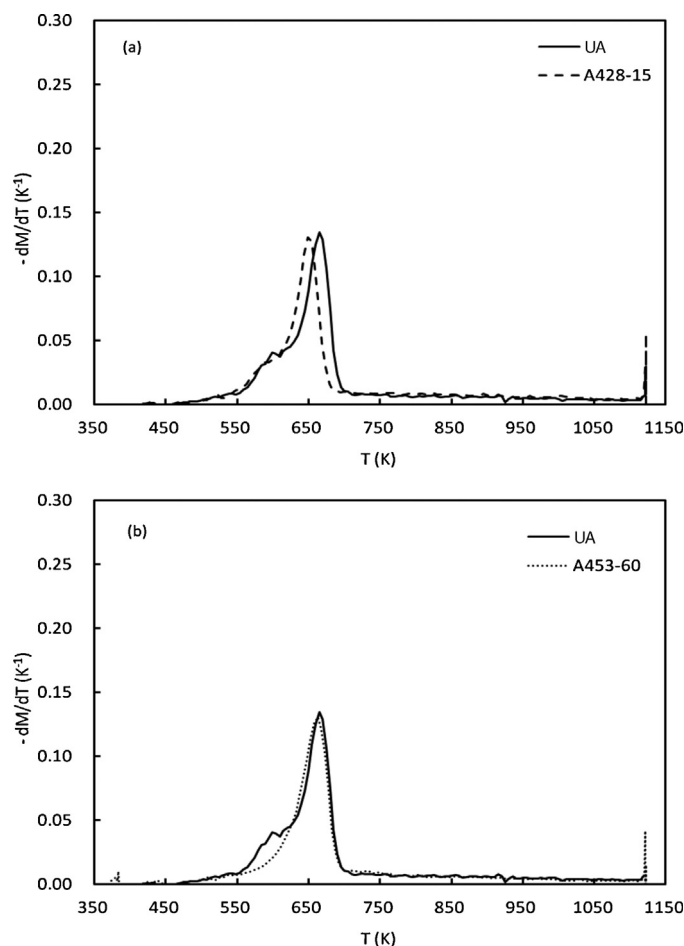


Fig. 6. DTG curves of autoclaved BCs. UA, HR: as specified in Fig. 5. (a) and (b) Cases A428-15, A453-60.

condition for Case A453-60 ($T = 453$ K, $t = 60$ min), its ultimate residue is higher than that of un-autoclaved raw BC as demonstrated in Fig. 5b. This is because of the low content of HC in the autoclaved BC of Case A453-60. A higher content of non-HC results in a higher residue after pyrolysis. The closed DTG curves for Cases A453-60 and UA as shown in Fig. 6b again indicate that the pyrolytic quality of BC after autoclaving at 453 K for 60 min is mainly preserved.

4. Concluding remarks

1. The dry-basis reductions of bamboo chopstick (BC) and its combustibles (CBs) increase as reaction time (t) and temperature (T) increase.
2. Vigorous autoclaving such as for the case at 453 K with 60 min results in the preservations of hemi-cellulose (HC), cellulose (CE) and lignin (LG) of 58.44, 83.35 and 81.50 wt.%, respectively.
3. For mild autoclaving, large portions of HC, CE and LG of BC of 74.29–93.91, 87.54–88.95 and 83.39–87.74 wt.% are still kept, maintaining the utilization properties of BC.
4. The proper conditions for the autoclaving of BC examined in this study are at 428 K and 60 min yielding product consisting of more CBs of 63.42 wt.% with 84.11 wt.% preservation of CBs while less ash and moisture of 0.73 wt.% and 35.85 wt.%, respectively.
5. The energy densification ratio of BC mildly increases to 1.06–1.17 after autoclaving.

6. The pyrolysis characteristics of autoclaved BCs under the conditions of this study are closed to that of un-autoclaved raw BC.

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